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INVESTIGATIONS ON LIGHT AND HEAT, PUBLISHED WITH APPROPRIATION FROM THE RUMFORD FUND.

XIV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF HARVARD UNIVERSITY.

PAPERS ON THERMO-ELECTRICITY.—No. I.

BY JOHN TROWBRIDGE AND CHARLES BINGHAM PENROSE.

Presented May 29th, 1883.

IN general we have, if σ denote the Thomson effect and T the temperature,

$$\int \sigma \, dT = 0.$$

There are, however, certain cases in which it appears that this integral is not zero. These cases occur when an abrupt variation of temperature takes place across any plane cutting the conductor. It is well to consider the problem from several points of view. Suppose a homogeneous circuit so heated that one part is maintained at the constant temperature T, and the rest at the temperature T_0, the change of temperature taking place at two planes which cut the conductor. The Thomson effect can only take place at these planes, and it is of opposite sign at each. The only heat effect, as far as we know, in this circuit, is the Thomson effect; if there is any electromotive force, we must have

$$E = \sigma_A - \sigma_B,$$

σ_A and σ_B being the effects at the planes.

From thermodynamic principles, it is obvious that the absorption must take place at the higher temperature T, and the evolution at T_0. The second law of thermodynamics gives

$$\frac{\sigma_A}{T} - \frac{\sigma_B}{T_0} = 0.$$

This equation shows that σ_A cannot equal σ_B, and in this special case of a homogeneous circuit there must be an electromotive force. We

also see that, at least for this case, the Thomson effect must be proportional to the absolute temperature.

To look at the problem from another point of view, suppose that in the homogeneous circuit there is but one abrupt change of temperature. That is, the temperature varies continuously from $T_0 — T_1$, and then falls abruptly to T_0. In this case the curve representing the change of temperature along the curve is discontinuous at T. The integral of σ throughout the circuit is then not necessarily zero. The part of the integral corresponding to the fall from $T — T_0$ has in this case the maximum or the minimum value of which it is capable. The complete effect through the circuit is represented by

$$\int_{T_1}^{T_0} \sigma + \sigma \, (T_1 - T_0).$$

If σ varies with the temperature, this expression cannot equal zero. If the current is in such a direction as to absorb heat at the plane of abrupt variation of temperature, the part of the general integral corresponding to the abrupt change has its maximum value; otherwise it has its minimum value. There is nothing in the equation to determine the direction of the current. Its intensity will obviously be the same in either direction,

$$\int_{T}^{T_0} \sigma \, dT$$

being a mean between its maximum and minimum values. We have tried several experiments to see if the direction of the current was related to the direction of the Thomson effect. It was soon perceived, however, that in the method employed many complicating causes masked the effect sought. From the fact that the equations show that a current can take place in either direction, we must conclude that there are most probably equal currents in opposite directions, making the resultant current equal zero. This is especially so in the perfectly symmetrical case first considered, where there are two abrupt changes of temperature. We are not aware that any experiments have been made on a circuit arranged in this way, and in fact it would be most difficult to realize the arrangement practically. In the second case, however, experiment shows that there is a current, and if there is anything in the nature of the metal which prevents the plane of abrupt variation of temperature from acting as the reservoir and refrigerator at the same time, then the equations explain the current. We

shall see that in special cases there is another heat effect at this plane; it is probable, therefore, that this effect exists in every case.

An abrupt variation of temperature can be produced practically in various ways. Le Roux and others have produced the currents by cutting a strip of metal in such a shape that its section varied abruptly from the broad to the narrow part. When a flame is applied to the narrow part, it becomes heated so much more rapidly than the broad portion that the temperature changes abruptly.

Maxwell says, in regard to these cases, that a current is produced in a homogeneous conductor when "at any part of the conductor a sensible variation of temperature occurs between points whose distance is within the limits of molecular action."

Le Roux attempts to explain the phenomena by a difference of pressure caused by the heat, the current being due to heating the contact of compressed and free parts of the same metal.

Becquerel produced an abrupt variation of temperature by suddenly uniting the hot and cold ends of a wire. The current in this case is, as Becquerel pointed out, at least partly due to a coating of oxide. In the case of lead the current is probably due to a coating of oxide, as the Thomson effect for lead is zero.

In the experiments made by us, with the object of observing whether there was any law connecting the direction of the current with that of the Thomson effect, the method of varying the section abruptly was employed. This method gets rid of all complications due to impurities at the surface of contact; but in cutting the metal to the necessary shape, the parts were necessarily more or less strained, and the results sought were always masked by a permanent current between the strained and unstrained parts. The direction of this current depended upon the position of the point where the heat was applied. The direction could be reversed by moving the lamp a few centimeters to either side, beneath the narrow part. The best method to avoid these complications is to pass a fine wire through the non-conducting partition separating the two compartments of a vessel, each compartment being filled with some good thermal conductor, and kept at different temperatures. This method has not yet been tried.

We have seen that the equations do not determine the direction of the thermo-electric current, and consequently that it is probable that a current exists in both directions. The Thomson effect, then, cannot alone explain the current that experiment shows to exist; there must be some other effect at the plane of abrupt variation. That this effect does take place in certain special cases there can be no doubt.

Tables of the values of the Thomson effect show that nickel changes twice between 175° and 340°. There are two points of deflection in the thermo-electric line. At these points, —

$$\frac{d}{dT}\left(\frac{\pi}{T}\right) = 0.$$

Let T_0 be the temperature at which the Thomson effect equals zero, and let T be a temperature above this. Let the circuit be so heated that the temperature rises gradually from $T_0 - T$, and then falls abruptly to T_0. Any heat effect at the plane must necessarily take place at the higher temperature, if we suppose the Thomson effect alone to exist. Hence from thermodynamic considerations the absorption must take place here. In this case the direction of the current is completely determined.

Suppose, now, we pass a current from some outside source, through the circuit, in such a direction as to absorb heat where the temperature falls gradually. There can be no evolution of heat at the plane, as it can take place neither at T_0 nor at T. If the whole energy of the current is expended in heat we must have

$$EI = RI^2 - I\int_T^{T_0} \sigma\, dT.$$

$$\therefore\ E = RI - \int_T^{T_0} \sigma\, dT.$$

That is, the electromotive force of the outside current is diminished by an electromotive force peculiar to the arrangement, and due to the absorption of heat in the circuit. But if the Thomson effect is the only effect in this circuit, the current produced by it does not obey the fundamental principles of thermodynamics. We have an engine, working between finite temperatures, in which there is no loss of heat.

Suppose, moreover, $T < T_0$, and pass a current in such a direction as to evolve heat where the temperature varies continuously. There can be no absorption at T_0, and

$$E = RI + \int \sigma\, dT.$$

In this case the outside electromotive force is increased by a secondary electromotive force. But unless some effect besides the Thomson effect exists, the secondary current is produced alone by an evolution of heat. The conclusion is absurd, and there must exist some other effect at the plane of abrupt variation. If this effect exists for the

special cases considered, it seems probable that it exists for all cases where there is a sensible variation of temperature between points whose distance is within the limits of molecular action. It obviously differs from both the Thomson and Peltier effects.

Several properties of this effect can easily be deduced. In the first place, since in general the current is caused entirely by it, — the Thomson effect producing equal and opposite electromotive forces, — if the effect obeys the ordinary thermodynamic laws, it must exist so as to cause an absorption and an evolution of heat at the plane of abrupt variation. This is not the only case of a thermodynamic arrangement where the evolution and absorption take place at one plane. In a thermo-electric circuit which has two neutral points, and in one metal of which the Thomson effect is null, if the two junctions are maintained respectively at the temperatures of the neutral points, all the heat effects take place in one metal, and if the circuit is so arranged that the change of temperature takes place across a plane, then all the effects occur at this plane.

If we call the new effect $\Phi(T)$, the general equations for a circuit where there exists one abrupt variation of temperature become: —

$$-\left[\int_{T_0}^{T_1} \sigma dT + \sigma_{T_1}(T_1 - T_0)\right] + \int_{T_1}^{T_0} \sigma dT + \sigma_{T_0}(T_0 - T_1) + \Phi(T_1) - \Phi(T_0) = E.$$

$$-\left[\int_{T_0}^{T_1} \frac{\sigma}{T} dT + \sigma_{T_1} \frac{T_1 - T_0}{T_1}\right] + \int_{T_1}^{T_0} \frac{\sigma}{T} dT + \sigma_{T_0} \frac{T_0 - T_1}{T_0} + \frac{\Phi(T_1)}{T_1} - \frac{\Phi(T_0)}{T_0} = 0.$$

The first parts of these equations are identically zero: —

$$\Phi(T_1) - \Phi(T_0) = E.$$

$$\frac{\Phi(T_1)}{T_1} - \frac{\Phi(T_0)}{T_0} = 0.$$

The latter equation shows that $\Phi(T)$ is proportional to T. The electromotive force is then proportional to the difference of temperature between the two surfaces of the plane.

The chief practical uses of thermo-electricity are in the measurement of high and low temperatures, and in the conversion of the energy of heat into that of an electric current. The measurement of

temperatures is much complicated by the existence of the two thermal effects, and by the fact that the direction of these effects is not constant for all ranges of temperature. The existence of the Thomson effect renders the curve of the electromotive forces and temperatures a parabola. The electromotive force cannot be considered proportional to the difference of temperatures of the junctions. Tait's ingenious method of acting on a differential galvanometer with two elements, gives an arrangement where the deflection is proportional to the difference of temperatures; but the method is exceedingly difficult in practice. We have also seen that, when an abrupt variation of temperature is produced, the electromotive force is probably proportional to the difference of temperatures; but there is no obvious method of realizing this arrangement practically for the measurement of temperature. The chief difficulty, however, in using the thermo-electric element as a thermometer, is due to the reversal of the heat effects. Every element must first be tested through the ranges in which it is to be used; and this testing necessitates the use of some other method of measuring temperatures, which is very difficult and inaccurate.

In regard to the use of the thermo-electric element as a heat engine, there is always a loss of heat, from two causes, which is absolutely unavoidable unless some substance can be procured which has a thermal conductivity of zero, and a finite electrical conductivity. This loss must always be taken into consideration in comparing the efficiency of the thermo-electric engine with that of other heat engines.

In a bar of section S, and length l, the quantity of heat lost in unit time by conduction is

$$H = K S \frac{t_2 - t_1}{l}.$$

That generated in unit time by a current of electricity is

$$H_1 = I^2 k \frac{l}{S} = E^2 S \frac{1}{k l}.$$

K and $\frac{1}{k}$ are the thermal and specific electrical conductivities. Loss of heat by radiation from the surface of the bar is supposed to be avoided. If this bar is supposed to form part of a thermo-electric element, any increase of S throughout the bar, that is, so as to increase the surfaces of contact, will increase $H + H_1$. If, however, the current strength is fixed, that is, if the current is passed through the bar from an outside circuit of large resistance compared with that of the

bar, we may consider I independent of S, and the sum of the heat lost is a minimum when

$$\frac{dH}{dS} + \frac{dH^1}{dS} = 0.$$

$$\therefore - I^2 k l \frac{1}{S^2} + K \frac{t_2 - t_1}{l} = 0.$$

$$\therefore S = Il \left(\frac{k}{K(t_2 - t_1)}\right)^{\frac{1}{2}}.$$

Substituting this value of S in H and H_1,

$$H = I [k K (t_2 - t_1)]^{\frac{1}{2}}, \quad \text{and} \quad H_1 = I [k K (t_2 - t_1)]^{\frac{1}{2}}.$$

That is, the heat dissipated is a minimum when that generated by the current per unit time is equal to that lost by conduction per unit time.

Within certain limits the thermo-electric engine follows the ordinary law of other heat engines: the work done increases as the difference between the temperatures of the hot and cold junctions increases. Unfortunately, however, the existence of neutral points renders it impossible to obtain an unlimited electro-motive force from a thermo-electric element. This appears to be one of the most serious objections to the practical use of thermo-electricity. We are at present engaged upon some experiments on the effect of high pressure and high temperature upon the position of the neutral point.